

Superconductivity of novel tin hydrides (Sn_nH_m) under pressure

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ABSTRACT

With the motivation of discovering high-temperature superconductors, evolutionary algorithm is employed to search for all stable compounds in the Sn-H system. In addition to the traditional SnH_4 , new hydrides SnH_8 , SnH_{12} and SnH_{14} are found to be thermodynamically stable at high pressure. Dynamical stability and superconductivity of tin-hydrides are systematically investigated. $\text{I}\bar{4}\text{m}2\text{-SnH}_8$, $\text{C}2/\text{m-SnH}_{12}$ and $\text{C}2/\text{m-SnH}_{14}$ exhibit higher superconducting transition temperatures of 81, 93 and 97 K compared to the traditional compound SnH_4 with T_c of 52 K at 200 GPa. An interesting bent H_3^- in $\text{I}\bar{4}\text{m}2\text{-SnH}_8$ and novel liner H_4^- in $\text{C}2/\text{m-SnH}_{12}$ are observed. All the new tin-hydrides remain metallic over their predicted range of stability. The intermediate-frequency wagging and bending vibrations have more contribution to electron-phonon coupling parameter than high-frequency stretching vibrations of H_2 and H_3 .

Introduction

Molecular hydrogen's phase transition to a metallic state has been subject of many experimental and theoretical studies.^{1,2} Although reaching the metallic state in pure solid hydrogen proved elusive, it is in the main focus of many groups and recently, the progress of bringing pure hydrogen to nearly 400 GPa has been reported.³⁻⁵ Following the pioneering work of Ashcroft,⁶ nearly room-temperature superconductivity was predicted in metallic molecular hydrogen.^{7,8}

An alternative approach in reaching enormous pressure to metalize hydrogen is to use chemical alloying as a means to exert additional pressure on hydrogen atoms.⁹ Hydrogen-rich compounds such as SiH_4 can be metalized at a much lower pressure.¹⁰ For metallic hydrogen, high Debye temperature and strong electron-phonon coupling are anticipated. The same is expected for hydrogen-rich compounds and it has been suggested that hydrogen-rich compounds are good candidates for high-temperature superconductivity.⁹ Theoretical studies confirm this idea with predicting high-temperature superconductivity in high-pressure hydrides such as H-Se,¹¹ Ca-H,¹² Sn-H,¹³ Pt-H¹⁴ and B-H.¹⁵ A series of hydrogen-rich compounds have been predicted to have remarkably high T_c values (e.g. 235 K for CaH_6 at 150 GPa,¹² 191 K for H_3S at 200 GPa,¹⁶ 64 K for GeH_4 at 220 GPa¹⁷) while the highest T_c that had been achieved experimentally was in the complex mercury cuprate (138 K at ambient pressure¹⁸ and 166 K at high pressures¹⁹). The new record of high T_c was established for H_3S , a compound whose existence and superconductivity at 200 K were first predicted theoretically¹⁶ in 2014 using USPEX and then observed experimentally²⁰ in 2015, and sparked a new wave of interest in hydrogen-rich superconductors.

In a previous theoretical study, Tse *et al.* reported a high-pressure metallic phase of SnH_4 with hexagonal $\text{P6}/\text{mmm}$ symmetry group, which is a layered structure intercalated with H_2 units, and superconducts close to 80 K at 120 GPa.²¹ Later, by using evolutionary algorithm, Gao *et al.*¹³ reported two novel low enthalpy metallic phases of SnH_4 with space groups $\text{P}6_3/\text{mmc}$ and $\text{Ama}2$, which both have hexagonal layers of Sn atoms with semi-molecular H_2 units. The reported stability ranges are 96-180 GPa for $\text{Ama}2$, and above 180 GPa for $\text{P}6_3/\text{mmc}$; with T_c values of 15-22 K at 120 GPa and 52-62 K at 200 GPa for $\text{Ama}2$ and $\text{P}6_3/\text{mmc}$, respectively.¹³

While SnH_4 was shown to be a relatively high- T_c superconductor, other tin hydrides were not explored so far. At the same

time, by now it is proven²² that totally unexpected compounds become stable under pressure, and that gives hope of finding even better superconductors. Hence, in this study, we systematically search for the stable compounds using the highly efficient method of variable-composition calculation (VCC). Apart from the previously reported phases of SnH₄, there is one metastable tetragonal phase of stannane with higher superconducting critical temperature. Other stable compounds e.g., SnH₈, SnH₁₂ and SnH₁₄ are found to form at high pressure with superconducting features. Moreover, we found a semi-molecular block of H₃⁻ species in the I $\bar{4}$ m2 structure of SnH₈. Novel H₄⁻ is also observed in C2/m-SnH₁₂. We predict a high T_c of 81 K at 220 GPa in the newly found compound SnH₈, 93 K for the phase SnH₁₂ at 250 GPa, 97 K for SnH₁₄ at 300 GPa and 91 K for the metastable phase of SnH₄ at 220 GPa.

Results

Evolutionary variable-composition calculations up to 20 atoms in the unit cell were performed at 150, 200, 250 and 300 GPa. To further investigate the newly found compounds, fixed-composition structure predictions for the most promising compounds were performed, with one to three formula units per cell. Candidate low-enthalpy structures obtained by analysis of predicted structures are as follow: metastable I4/mmm-SnH₄, stable I $\bar{4}$ m2-SnH₈, C2/m-SnH₁₂ and C2/m-SnH₁₄. In the I $\bar{4}$ m2-SnH₈ structure predicted at 220 GPa, Sn atoms are packed between where H₂ and H₃ semi-molecules are located, in which the surrounding bent H₃ units are aligned perpendicular to one another with nearest distance of 1.347 Å. In the C2/m-SnH₁₂, Sn atoms form a hexagonal packing intercalated with blocks of H₂ and H₄ semi-molecules.

Figure 1(a). shows the formation enthalpy (ΔH) of Sn-H compounds at the chosen pressures. Significantly, in addition to reproducing various structures of solid SnH₄,^{13,21} Sn²³ and H₂,²⁴ novel compounds SnH₈, SnH₁₂ and SnH₁₄ are found to be stable in a wide pressure range in our systematic evolutionary structure search. It can be seen from Fig. 1(a). that at around 200 GPa the tetragonal SnH₈ with the space group of I $\bar{4}$ m2 lies above the tie-line, therefore, is metastable with respect to the decomposition to P6₃/mmc-SnH₄ and C2/c-H₂. Between 150 to 300 GPa, we predict stable phases of H₂, SnH₄, SnH₈, SnH₁₂, SnH₁₄ and Sn.²³ Some metastable forms of SnH₆, SnH₉ and SnH₁₆ are also shown in Fig. 1(a). with open symbols.

SnH₄ is stable starting from 108 GPa as was predicted in previous report.¹³ It goes through a phase transition at 160 GPa. The higher pressure of 220 GPa favors stabilization of SnH₈. SnH₁₂ and SnH₁₄ reach stability at the pressures of 250 GPa and 280 GPa, respectively, and remain stable at least up to 300 GPa. The structures of SnH_n compounds are found to be dynamically stable within pressure ranges of their stability. Phonon band structures and phonon densities of states (PHDOS) are provided in Fig. 3. In the I $\bar{4}$ m2-SnH₈ structure, Sn atoms occupy the crystallographic 2a site and the H atoms are on the 4e, 8i and 4f sites (more structure information are provided in Table 1).

We checked the effects of zero-point energy using the quasi-harmonic approximation²⁵ at 250 GPa. The inclusion of zero-point noticeably lowered the formation enthalpy of SnH₈ with respect to SnH₄ and H₂ (Fig. 1(a)), implying that this compound can be formed at lower pressure. Consequently, SnH₁₂ lies above the hull, suggesting more pressure is needed to stabilize C2/m-SnH₁₂. In accord with what we expect, zero-point energy does not change the topology of the phase diagram, but shifts transition pressures.

In I $\bar{4}$ m2-SnH₈ structure, the ordered H atoms are split into two categories. One of H categories consists blocks of H₃ semi-molecules, which was previously observed in solid phases of BaH₆,²⁶ in an unstable structure of H₅Br ([H₃]Br[H₂]),²⁷ and in an intriguing linear form of H₃ with the bond length of 0.92 Å and strong covalent bonds with ELF magnitude of 0.8 in the H₅Te₂.²⁸

In contrast to H₅Br, which has approximately an equilateral triangle form of H₃, here we report the formation of H₃ in a bent molecule with the angle of 146.2° and bond length of 0.867 Å at 220 GPa in the I $\bar{4}$ m2 structure. The other H category forms in semi-molecular H₂ units, which are aligned parallel to each other.

The presence of different types of hydrogen can be explained based on charge transfer from Sn atom to each groups of hydrogen (H₂ or H₃). I $\bar{4}$ m2 structure consists of a [H₂][H₃]Sn[H₃] as shown in Fig. 2(a),(b). The bond length in H₃ unit is 0.867 Å, whereas H₂ has a longer bond length of 0.873 Å. Contrary to isolated H₂ that already has a filled σ bond resulting in a strong covalent bond, in the H₂ and H₃ semi-molecules, anti-bonding electrons cause lengthening of the bond, subsequently resulting in a weaker covalent bond. The slightly longer H-H bond length compared to isolated H₂ molecule (0.74 Å) is caused by charge transfer of 0.42 e⁻ and 0.48 e⁻ from Sn to each H₂ and H₃ units, respectively. Charge transfer is explained as an important factor in the formation of H₂ and H₃ blocks in the H₄Te, GeH₄, SnH₄, CaH₆, H₅Te₂, H₅Br, BaH₆^{12,17,26-28}

Analysis of electron localization function (ELF) shows a high ELF value of 0.88 between H atoms within the unit, indicating strong covalent bonding features (Fig. 2(e)). Fig. 2(e) indicated ELF magnitude of 0.37, pertaining to no covalent bond between Sn and hydrogen atoms.

In C2/m-SnH₁₂, intriguing formation of novel H₄ semi-molecules is observed; at 250 GPa, the distance between blocks of H₂ is 0.9916 Å. Higher pressure of 300 GPa decreases the distance to 0.8823 Å, leading to a strong covalent bond in the H₄⁻ units. Fig. 2(f). demonstrates the strength of covalent bonds in the linear H₄ units with the ELF magnitude of 0.85.

Electronic band structure of $\bar{I}4m2$ -SnH₈ is depicted in Fig. 4. Occurrence of flat and steep bands near the Fermi level has been suggested as a condition for enhancing electron-phonon coupling and the formation of Cooper pairs.

The calculated phonon dispersion curves and phonon density of states for $\bar{I}4m2$ structure of SnH₈ at 220 GPa is shown in Fig. 3(a). Dynamical stability is clearly evidenced by the absence of any imaginary frequencies in the whole Brillouin zone. The low-frequency bands below 250 cm⁻¹ are mainly from the vibration of Sn atoms. Modes between 300 and 1700 cm⁻¹ are mainly from the H-H wagging vibrations, and higher frequency vibrations above 2300 cm⁻¹ are due to H-H stretching vibrations in H₂ and H₃ units.

Low-frequency translational vibrations, mostly from Sn atom, contribute 23.7% (9.2%) to the total λ . Intermediate H-H wagging vibrations make a significant section of 65.7% (67.9%), and the rest is from stretching H vibrations, which contributes 10.6% (22.9%) for SnH₈ (SnH₁₂). It is different from the superconductivity in the Cmcm-H₂Br,²⁷ where Br translational vibrations contribute most to the total λ and similar to the $R\bar{3}m$ -H₄Te²⁸ and P4/mmm-BaH₆,²⁶ where medium-frequency H-wagging and bending modes contribute the most to the EPC. In accord with our expectation, λ increases almost linearly with the hydrogen content, where we found 60.2%, 72.2% and 77.1% contribution of H vibrations to the total λ of SnH₄, SnH₈ and SnH₁₂, respectively. This denotes the dominant role of H in the superconductivity of H-rich compounds.

The EPC calculations were performed to explore the superconductivity, in specific EPC constant λ , the Eliashberg phonon spectral function $\alpha^2F(\omega)$ and the logarithmic average of phonon frequencies ω_{log} (see Fig. 3.). We can calculate T_c based on the spectral function $\alpha^2F(\omega)$ and taking advantage of Allen-Dynes modified McMillan equation (Eq. 1.) by using Coulomb pseudo-potential μ^* of 0.10 and 0.13 as widely accepted values (see Table 2).

At 220 GPa, the predicted T_c values for $\bar{I}4m2$ -SnH₈ are 81 K and 72 K using μ^* values of 0.10 and 0.13, respectively. The calculated T_c slightly decreases with pressure (82 K at 200 GPa and 79 K at 300 GPa using $\mu^* = 0.10$) with a pressure coefficient of -0.023 K/GPa ($\frac{dT_c}{dP}$). Reported λ is comparable to the H₃Se ($\lambda = 1.09$) at 200 GPa,¹¹ but in $\bar{I}4m2$ -SnH₈ structure, we have reduced $\langle\omega_{log}\rangle$ of 919 K (1477 K for H₃Se), resulting in a lower T_c value.

In conclusion, we explored the energetically stable/metastable high-pressure phases of the Sn-H system in detail by means of *ab initio* evolutionary structure prediction. The results demonstrate that SnH₈, SnH₁₂ and SnH₁₄, reported for the first time in this work, are thermodynamically stable compounds that coexist stably with solid Sn, H₂ and SnH₄ in a wide pressure range starting from 220 to at least 300 GPa.

EPC calculations indicate that high-pressure SnH₈, SnH₁₂ and SnH₁₄ are phonon-mediated superconductors with T_c values of 81.3, 93.2 and 97.2 K, respectively. T_c decreases slightly with a rate of -0.023 K/GPa for $\bar{I}4m2$ -SnH₈ structure. λ is high for SnH_n compounds, comparable with H₃M-Im $\bar{3}m$, where M = S and Se.¹¹ Structures of SnH_n compounds contain linear and non-linear H₂⁻, H₃⁻ and H₄⁻ anions. Further experimental studies on the formation of SnH_n, n = 8, 12 and 14 at high pressure are needed, and these studies will serve as a guide for future experiments.

Methods

To find stable and low-enthalpy metastable structures, we took advantage of evolutionary algorithm implemented in USPEX code,²⁹⁻³¹ which has been extensively used to predict stable crystal structures with just a knowledge of the chemical composition and without any experimental information.^{15,32,33}

In this method, the initial generation of structures and compositions is produced randomly with using random space group from the total list of 230 groups. In order to find all stable stoichiometric compounds and the corresponding stable and metastable structures in the Sn-H binary system, we used VCC method implemented in USPEX.^{29,30}

Structure relaxations were carried out using VASP package³⁴ in the framework of Density Functional Theory (DFT) adopting PBE-GGA (Perdew-Burke-Ernzerhof generalized gradient approximation).³⁵ The projector augmented-wave approach (PAW)³⁶ was used to describe the core electrons and their effects on valence orbitals. The plane-wave kinetic energy cutoff was chosen as 1000 eV, and we used Γ -centered uniform k-points meshes to sample the Brillouin zone.

Phonons and thermodynamic properties of Sn-H compounds are calculated using the PHONOPY package.^{25,37} The supercell approach is used with simulation cell dimensions greater than 10 Å (typically 3 × 3 × 3 representation of the primitive cell). We used valence electron configuration of 4d¹⁰ 5s² 5p² and 1s¹ for tin and hydrogen, respectively. Phonon frequencies and electron-phonon coupling (EPC) coefficients are calculated using DFPT as implemented in the QUANTUM ESPRESSO (QE) code.³⁸ In the QE calculations, we employed ultrasoft pseudopotentials along with PBE exchange and correlation functional.³⁵ A plane-wave basis set with a cutoff of 70 Ry gave a convergence in energy with a precision of 1 meV/atom. The EPC parameter was calculated using 4 × 4 × 3, 5 × 5 × 4 and 5 × 5 × 4 *q*-point meshes for $\bar{I}4m2$ -SnH₈, C2/m-SnH₁₂ and C2/m-SnH₁₄, respectively. Denser *k*-point meshes, 8 × 8 × 6, 10 × 10 × 8 and 10 × 10 × 8 were used for convergence checks for the EPC parameter λ . The superconducting T_c , was estimated using the Allen-Dynes modified

McMillan equation:³⁹

$$T_c = \frac{\omega_{log}}{1.2} \exp\left(\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right) \quad (1)$$

where ω_{log} is the logarithmic average frequency and μ^* is the Coulomb pseudopotential, for which we used 0.10 and 0.13 values, which often give realistic results. The EPC constant and ω_{log} were calculated as:

$$\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega \quad (2)$$

and

$$\omega_{log} = \exp\left[\frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega)\right] \quad (3)$$

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Author contributions

M.M.D.E. performed all the calculations presented in this article with help from Z.W., Q.Z. and H.D. Research was designed by A.R.O. S.W, M. R. and X-F. Z. analyzed data. M.M.D.E., A.R.O. and Z.W. wrote the first draft of the paper and all authors contributed to revisions.

Additional information

Competing financial interests: The authors declare no competing financial interests.

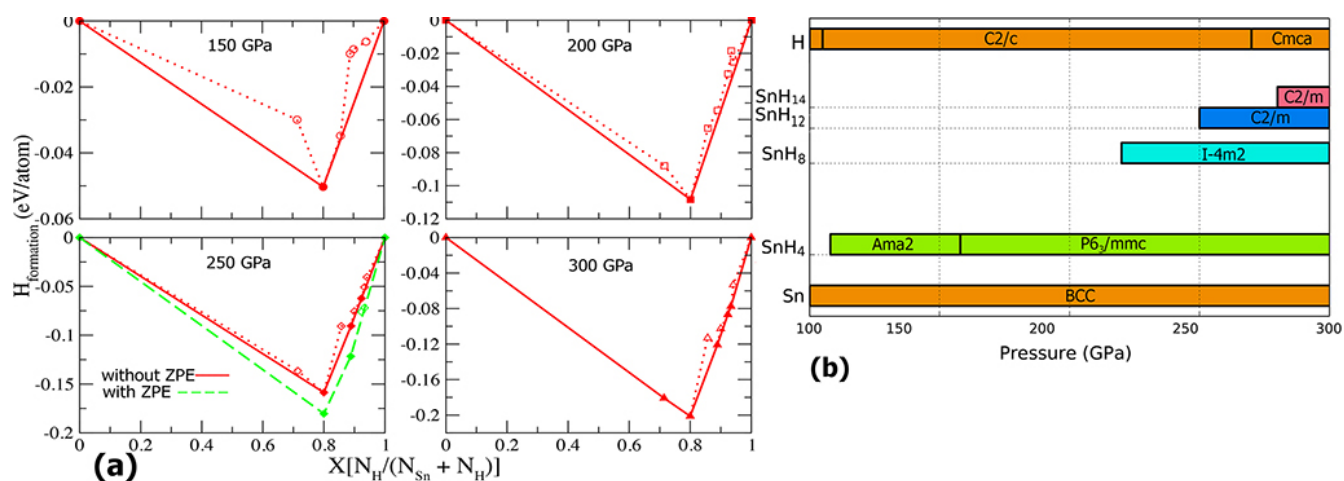


Figure 1. Thermodynamics of the Sn-H system. (a) Predicted formation enthalpy of Sn_nH_m compounds with respect to decomposition into constituent elemental Sn and H_2 at different pressures. Red dashed lines connect data points, solid red lines denote the convex hull and green dashed line shows the effect of ZPE inclusion at 250 GPa. (b) Predicted pressure-composition phase diagram of Sn-H compounds.

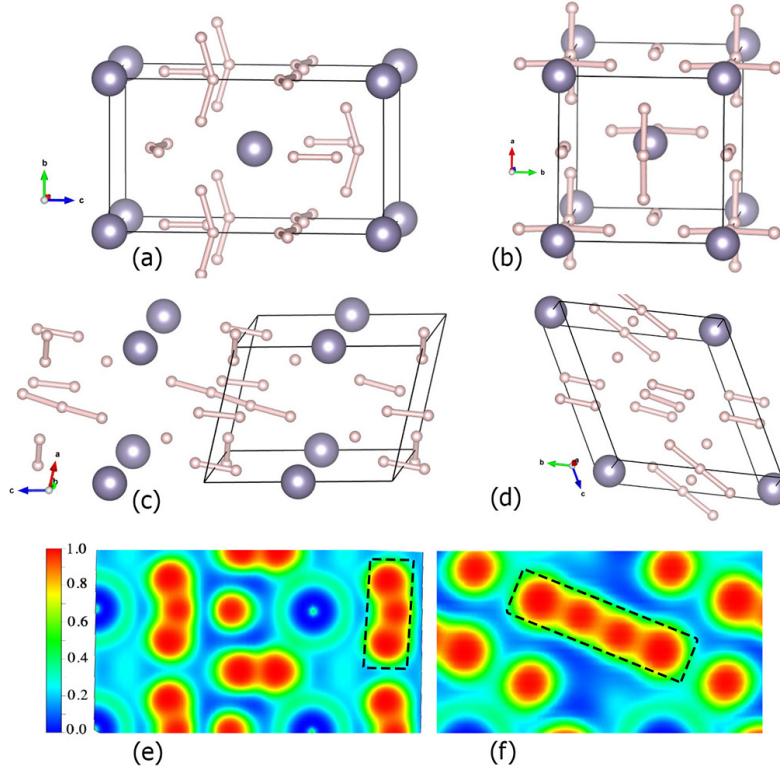


Figure 2. Predicted structures of (a),(b) SnH_8 [$\bar{1}4m2$], (c) SnH_{12} [C2/m] and (d) SnH_{14} [C2/m]. Large and small spheres represent Sn and H atoms, respectively. Electron localization functions (ELF) for (e) SnH_8 [$\bar{1}4m2$] at 220 GPa and (f) SnH_{12} [C2/m] at 250 GPa.

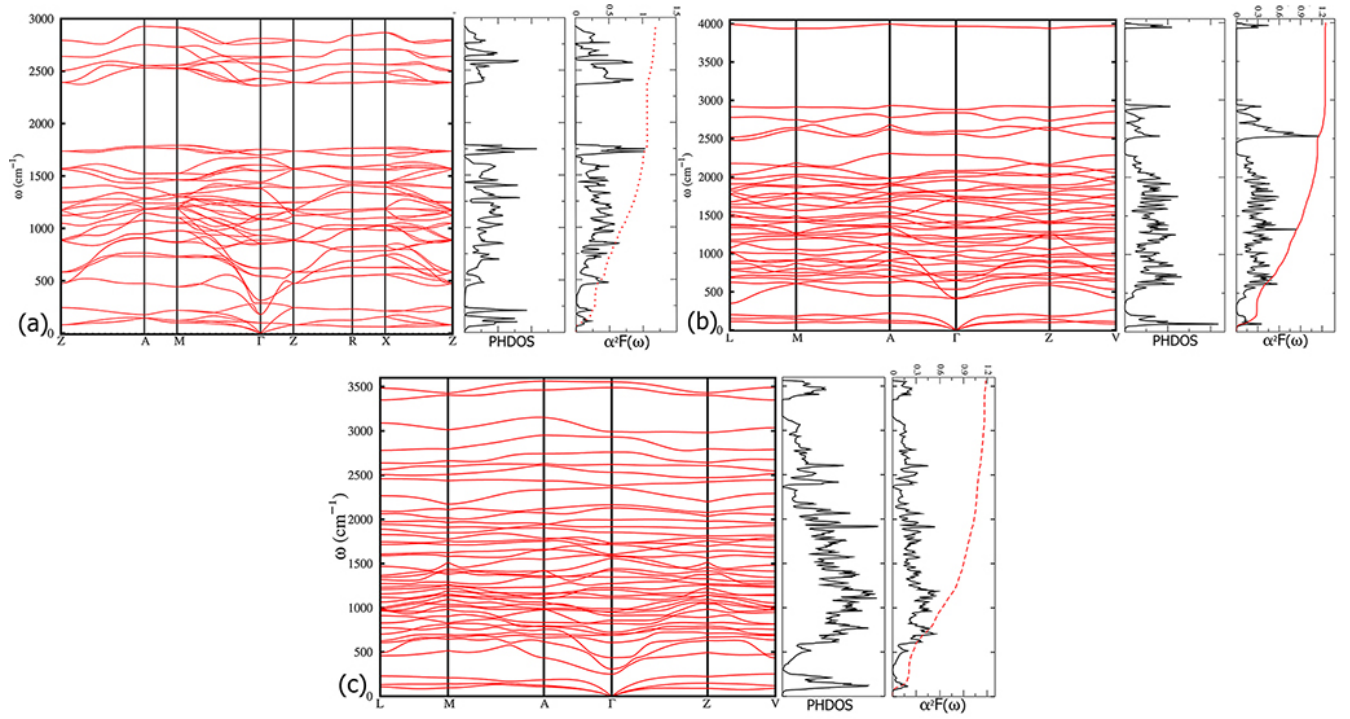


Figure 3. Phonon band structure, PHDOS, Eliashberg phonon spectral function $\alpha^2F(\omega)$ and electron-phonon integral $\lambda(\omega)$ of: (a) SnH_8 [$\bar{1}4m2$] at 220 GPa, (b) SnH_{12} [C2/m] at 250 GPa and (c) SnH_{14} [C2/m] at 300 GPa.

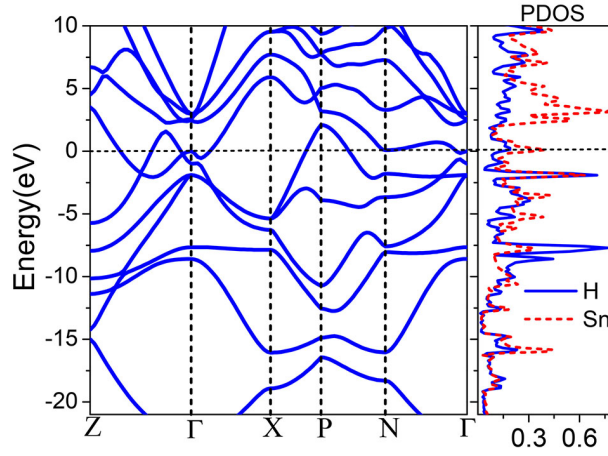


Figure 4. Electronic band structure and projected DOS on Sn and H atoms for SnH₈ [$\bar{I}4m2$] at 220 GPa.

Table 1. Lattice parameters and atomic coordinates for SnH₈, SnH₁₂ and SnH₁₄ at 220, 250 and 300 GPa, respectively.

Space group	Lattice parameters	Atom	x	y	z
$\bar{I}4m2$ SnH ₈	a=3.076 Å	Sn(2a)	0.0000	0.0000	0.0000
	c=5.523 Å	H ₁ (8i)	0.2729	0.0000	0.3331
	at 220 GPa	H ₂ (4e)	0.0000	0.0000	0.6208
		H ₃ (4f)	0.0000	0.5000	0.1701
C2/m SnH ₁₂	a=5.191 Å	Sn(2d)	0.0000	0.5000	0.5000
	b=3.065 Å	H ₁ (4i)	0.0495	0.0000	0.6553
	c=7.388 Å	H ₂ (4i)	0.4564	0.0000	0.7226
	$\beta=148.95^\circ$	H ₃ (4i)	0.3428	0.0000	0.8832
	at 250 GPa	H ₄ (8i)	0.3810	0.2399	0.1123
C2/m SnH ₁₄	a=7.129 Å b=2.730 Å c=3.673 Å $\beta=60.71^\circ$	H ₅ (4g)	0.0000	0.1233	0.0000
		Sn(2b)	0.0000	0.5000	0.0000
		H ₁ (4i)	0.3651	0.0000	0.7031
		H ₂ (4i)	0.1857	0.0000	0.9852
	at 300 GPa	H ₃ (4i)	0.0732	0.0000	0.6252
		H ₄ (4i)	0.8063	0.0000	0.8090
		H ₅ (8i)	0.2365	0.2808	0.4035
		H ₆ (2d)	0.0000	0.5000	0.5000
		H ₇ (2c)	0.0000	0.0000	0.5000

Table 2. The calculated EPC parameter (λ), logarithmic average phonon frequency (ω_{log}) and critical temperature (T_c) (with $\mu^* = 0.10$ and 0.13) for metastable SnH_4 , stable SnH_8 , SnH_{12} and SnH_{14} at 220, 220, 250 and 300 GPa, respectively.

Structure	Pressure (GPa)	λ	ω_{log} (K)	T_c (K)
I4/mmm SnH ₄	220	1.180	1025	91 ($\mu^*=0.10$)
				80 ($\mu^*=0.13$)
I4m2-SnH ₈	220	1.188	919	81 ($\mu^*=0.10$)
				72 ($\mu^*=0.13$)
C2/m-SnH ₁₂	250	1.250	991	93 ($\mu^*=0.10$)
				83 ($\mu^*=0.13$)
C2/m-SnH ₁₄	300	1.187	1099	97 ($\mu^*=0.10$)
				86 ($\mu^*=0.13$)